

# Spatial distribution of PM<sub>2.5</sub> associated organic compounds in central California

Lynn R. Rinehart<sup>a,1</sup>, Eric M. Fujita<sup>a</sup>, Judith C. Chow<sup>a</sup>,  
Karen Magliano<sup>b</sup>, Barbara Zielinska<sup>a,\*</sup>

<sup>a</sup>Desert Research Institute, Department of Atmospheric Science, 2215 Raggio Parkway, Reno, NV 89512, USA

<sup>b</sup>California Air Resources Board, 1001 I Street P.O. Box 2815, Sacramento, CA 95812, USA

Received 14 March 2005; received in revised form 19 September 2005; accepted 19 September 2005

## Abstract

As part of the California Regional PM<sub>2.5</sub>/PM<sub>10</sub> Air Quality Study, annual average concentrations of PM<sub>2.5</sub> associated organic compounds were measured using filter samples collected every sixth day for 24 h for 1 year. During this time many central California sites had 24-h PM<sub>2.5</sub> mass concentrations exceeding the National Ambient Air Quality Standard of 65 µg m<sup>-3</sup>. The highest concentration of 175 µg m<sup>-3</sup> was recorded in Fresno on January 1, 2001. Organic speciation of 20 sites within and near the central California valley provides a measure of the spatial differences of emission sources through the use of organic molecular markers. Additionally, it provides an opportunity evaluate their utility at ambient concentrations to measure the influence of emission sources at rural and urban locations. The most abundant particulate phase organic compounds identified were polar organic compounds. Sugar anhydrides, molecular markers of wood combustion, constituted the largest weight fraction of total carbon, followed by alkanic acids, and alkanedioic acids. Local emission sources such as residential wood combustion, gasoline and diesel vehicles were distinguished by unique molecular markers and found to vary among the annual average sites. The annual average concentrations of individual organic species within compound classes were observed to be highly correlated for many of the central California sites. The two Fresno sites were highly correlated to each other especially with respect to polycyclic aromatic hydrocarbons, but not well correlated to other sites.

© 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Levoglucosan; Polycyclic aromatic hydrocarbons; Polar organic compounds; Organic speciation; Biomass combustion; Trimethylsilylation; Fresno; CRPAQS

## 1. Introduction

The central valley of California is a low-elevation geographic basin surrounded by mountainous

terrain (Fig. 1). The lower portion of the valley, is in nonattainment of PM<sub>2.5</sub> and PM<sub>10</sub> standards (EPA, 2005). During the winter, PM concentrations in Fresno, CA often exceed the 24-h PM<sub>2.5</sub> National Ambient Air Quality Standard (NAAQS) of 65 µg m<sup>-3</sup> with gravimetric mass concentrations 2–3 times higher than the standard (Watson and Chow, 2002b). Major particulate emission sources include agricultural activities, biomass burning,

\*Corresponding author. Fax: +1 775 674 7060.

E-mail address: [Barbara.Zielinska@dri.edu](mailto:Barbara.Zielinska@dri.edu) (B. Zielinska).

<sup>1</sup>Currently at Colorado State University, Department of Atmospheric Science, Fort Collins, CO 80523, USA.

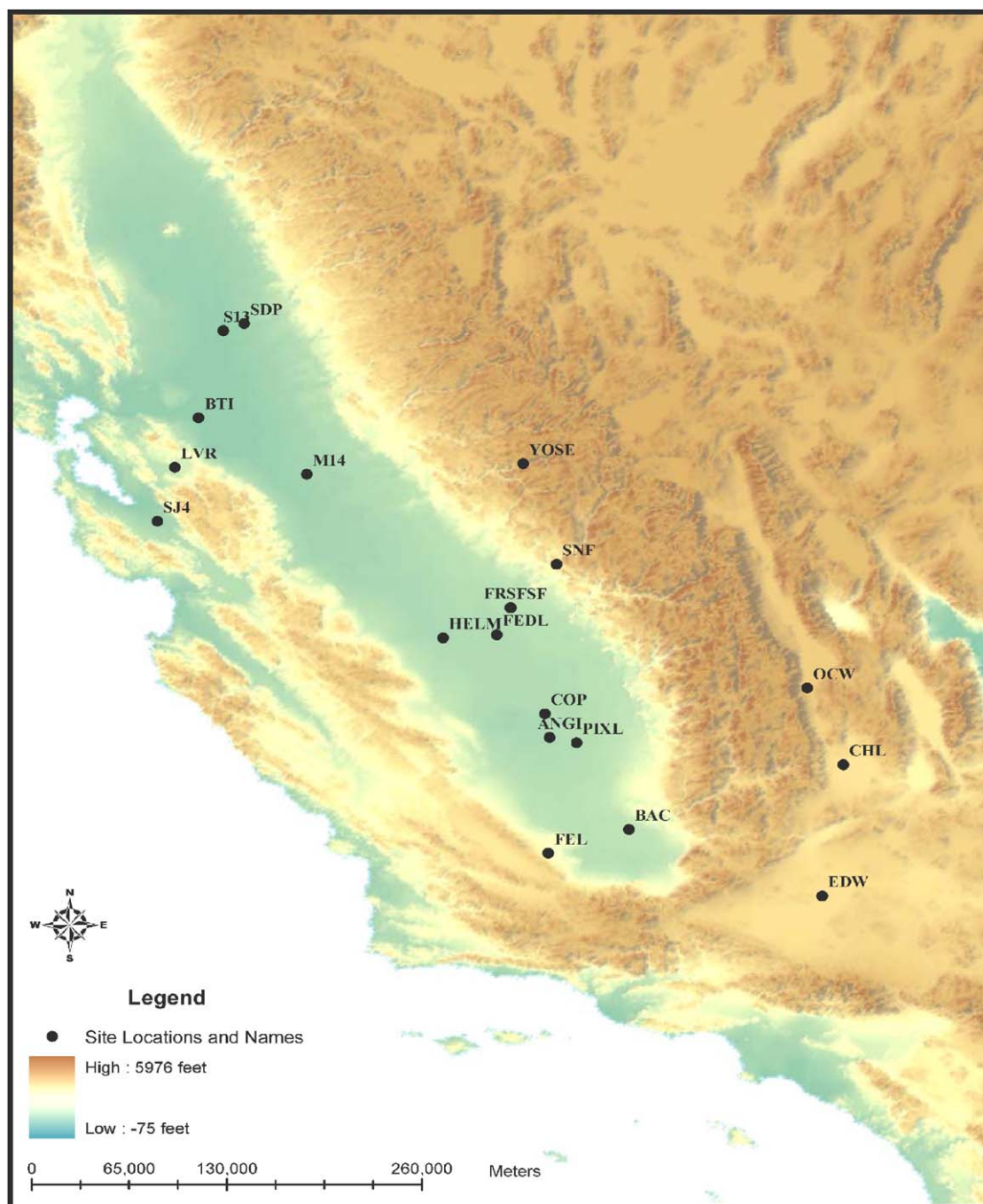


Fig. 1. Map of central California with the annual average sites.

cooking, on-road and off-road engine exhaust and oil refinement.

As part of the California Regional  $PM_{2.5}/PM_{10}$  Air Quality Study (CRPAQS), organic characterization of annual average samples was conducted for 20 sites to examine the spatial distribution of

$PM_{2.5}$  pollutants for the region and their relationships to urban and rural emissions. A few sites were located just outside the central valley to characterize regional background concentrations. A previous study, regarding spatial variability in urban areas in the US, revealed a higher variability in  $PM_{2.5}$  mass

concentrations among western sites than eastern sites (Pinto et al., 2004). A high fraction of central California PM<sub>2.5</sub> mass is carbonaceous material (Schauer and Cass, 2000; Watson and Chow, 2002a). Very few other studies have conducted a detailed organic speciation study with high spatial resolution. One study was conducted in the Los Angeles Air Basin, which included measurements of organic compounds for 12 southern California sites (Manchester-Neesvig et al., 2003) and found excellent agreement between two co-located samplers for organic speciation. Central California provides a unique opportunity to examine PM<sub>2.5</sub> organic composition for several sites within one topographically “isolated” region. Major air flow patterns for the valley are northwesterly with marine air entering the valley through the San Francisco bay area, which splits north toward the Sacramento valley and south to the San Joaquin Valley. Up-slope and down-slope winds occur along the valley foothills. However, heavily forested areas are generally far enough upslope to be mostly free of fresh urban pollution.

The objective of this paper is to examine and illustrate the spatial distribution, of particle-associated organic compounds for the 20 sites. The spatial characterization of these sites is important for elucidation of potential molecular markers for emission sources relative to urban, rural, and intra-basin sites.

## 2. Experimental section

### 2.1. Sample collection

Samples were collected at the annual average sites every sixth day for 24 h from February 1, 2000 to January 31, 2001 using Mini-Vol Portable Air Samplers (AirMetrics). The 20 sites include two sites in Fresno (FSF and FRS), two sites in Sacramento (S13 and SDP), Bethel Island (BTI), San Jose (SJ4), Modesto (M14), Bakersfield (BAC), and several rural sites including Angiola (ANGI), Helm (HELM), Feedlot (FEDL), Olancho (OCW), Pixely Wildlife Refuge (PIXL), Yosemite National Park (YOSE) and a site in the Sierra Nevada Foothills (SNF) near Auberry. The sites are associated with sampling objectives listed in Table 1 and shown in Fig. 1. Battery-powered Mini-Vol Portable Air Samplers (Air Metrics) were used to collect particles on filters in a cassette, which was equipped with impactors to exclude particles

larger than 2.5 µm in diameter with a nominal sampling flow rate of 5 L min<sup>-1</sup>. Organic compounds were analyzed from samples collected on Teflon-impregnated glass fiber filters (TIGF) (Pall-Gelman, 47 mm). During the same sampling period 24 h samples were also collected for gravimetric analysis of PM<sub>2.5</sub> mass on Teflon filters (Pall-Gelman, 47 mm) and for thermal optical carbon analysis on quartz-fiber filters (Pall-Gelman, 47 mm, heat treated) at 16 of the 20 sites where samples were collected for organic analysis. Prior to sampling, TIGF filters were pre-cleaned by sonication for 10 min in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) twice followed by methanol (CH<sub>3</sub>OH), with the solvent replaced and drained each time. Filters were then dried in a vacuum oven at -20 inches of Hg and 50 °C, for a minimum of 24 h, wrapped in aluminum foil that had been pre-fired at 500 °C for 4 h, placed in Uline metallic Zip-Top static shielding bags, and stored at room temperature. An aliquot of each batch of cleaned TIGF filters was extracted, and checked by GC/MS for purity. Filters were loaded into cassettes in the laboratory shipped to the field packed with ice to avoid contamination. After sampling, filters were immediately refrigerated and kept cold during overnight shipping. Samples were archived in a freezer until analysis.

### 2.2. Analytical methods

Carbon analysis was conducted using the IMPROVE protocol (Chow et al., 1993). For organic compound speciation all of TIGF filters for the year were combined for each site and extracted by accelerated solvent extraction (Dionex ASE 300 Accelerated Solvent Extrator) with dichloromethane followed by acetone to expand the polarity range of analytes. These extracts were then combined and concentrated by rotary evaporation followed by moisture-filtered ultra high purity (UHP) nitrogen blow down and then split into two fractions. The first fraction was analyzed without further alteration for polycyclic aromatic hydrocarbons (PAH), alkanes, hopanes, and steranes by gas chromatography coupled with mass spectrometry (GC/MS). The samples were analyzed by electron impact (EI) GC/MS using a Varian CP-3800 gas chromatograph equipped with a 8200 CX Auto-sampler and interfaced to a Varian Saturn 2000 Ion Trap Mass Spectrometer. Analysis of the PAHs, hopanes, steranes and the internal standards added were described previously (Zielinska et al.,

Table 1  
The 20 annual average sites

ID	Site name	Site type
ANGI	Angiola	Intrabasin Gradient
BAC	Bakersfield California Avenue	Residential and Traffic
BTI	Bethel Island	Residential and Traffic
CHL	China Lake	Regional Background and Traffic
COP	Corcoran	Residential and School Buses
EDW	Edwards Air Force Base	Intrabasin Gradient
FEDL	Dairy (near Raisin City)	Agricultural Operations: Dairy Farm
FEL	Fellows	Commercial: Oil Fields
FRS	Fresno Residential	Residential
FSF	Fresno First St (Supersite)	Residential and Commercial
HELM	Helm	Agricultural Operations: Cotton Fields
LVR	Livermore	Residential and Commercial
M14	Modesto	Residential
OCW	Olancho	Regional Background and Traffic
PIXL	Pixely Wildlife Refuge	Intrabasin Gradient
S13	Sacramento T Street	Residential and Commercial
SDP	Sacramento Del Paso	Residential
SJ4	San Jose 4th Street	Residential and Traffic
SNF	Sierra Nevada Foothills	Residential and Commercial
YOSE	Yosemite	Regional Background and Traffic

2004a, b). The second fraction was evaporated to 100 µl under moisture-filtered UHP nitrogen and transferred to 300 µl silanized glass inserts (National Scientific Company, Inc.). Samples were further evaporated to 50 µl and 25 µl of pyridine, 25 µl of additional internal standards, and 150 µl of BSTFA with 1% TMCS [*N*, *O*-bis (trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane (Pierce)] were added. These derivatizing reagents convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids, methoxyphenols, cholesterol, sitosterol, and levoglucosan. The glass insert containing the sample was put into a 2 ml vial and sealed. The sample was then placed into a thermal plate (custom made) containing individual vial wells at 70 °C for 3 h. The calibration solutions were freshly prepared and derivatized just prior to the analysis of each sample set, and then all samples

were analyzed by GC/MS within 18 h to avoid degradation. The samples were analyzed by chemical ionization (CI) GC/MS technique with isobutane as a reagent gas using a Varian CP-3400 gas chromatograph with a model CP-8400 Auto-sampler and interfaced to a Saturn 2000 Ion Trap Mass Spectrometer. Analysis of the polar organic compounds (POC) and the internal standards added were described previously (El-Zanan et al., 2005).

The measurement uncertainties associated with each individual compound is defined by analyte

uncertainty =  $\sqrt{(\text{precision} \times \text{concentration})^2 + (\text{MDL})^2}$ , where MDL is the method detection limit (Bevington, 1969). This equation incorporates the analyte detection limit for each compound so when concentrations approach zero, the error is reported as the analyte detection limit. Analytical precision was measured directly by replicate analysis of 21 duplicate analyses as part of the whole CRPAQS database.

Results are reported after blank subtraction with a composite field blank of 60 individual field blanks from the 20 sites which were treated identically as above.

### 3. Results and discussion

#### 3.1. $PM_{2.5}$ trends for select sites

During the study period several exceedances of the  $PM_{2.5}$  24-h NAAQS were recorded. The maximum 24-h mass concentration reached  $175 \mu\text{g m}^{-3}$  on January 1, 2001 at FSF. There were a total of 34 exceedances of the 24-h NAAQS recorded for 13 of the 20 sites (some sites were excluded due to missing values). 16 of the 34 exceedances occurred at the two Fresno sites (supersite FSF and residential FRS) on corresponding days, while four exceedances occurred at M14, and four exceedances at PIXL. A few exceedances occurred in COP (3), SDP (2), and FEL (2) sites, while only one exceedance each was recorded at LVR, BTI, and HELM sites. All exceedances occurred within the same time period(s) suggesting valley-wide meteorological conditions for pollution stagnation and build-up. Shown in Table 2 are the arithmetic means of mass and carbon concentrations for the full year and the late fall and early winter season.

Mass concentrations were highest in late fall and early winter months, October through January, as expected from the stronger seasonal temperature



Table 2

Seasonal influences of mass and total carbon concentrations for the annual average sites

Site	Annual average $\mu\text{g m}^{-3}$		Fall-winter average <sup>a</sup> $\mu\text{g m}^{-3}$		Percent seasonal contribution <sup>b</sup>	
	Mass	Total carbon	Mass	Total carbon	Mass	Total carbon
BTI	8.57	4.08	18.2	5.69	68.5	43.3
CHL	2.29	3.81	1.54	0.90	20.8	9.18
COP	18.5	6.82	36.0	8.20	69.2	42.8
FEL	13.1	5.04	24.4	3.22	68.8	23.1
FRS	24.2	11.3	50.4	18.4	75.1	58.1
FSF	25.3	13.6	54.2	22.6	76.7	56.8
HELM	12.0	5.03	24.8	4.74	71.3	34.3
LVR	10.8	6.80	20.5	9.86	63.4	50.8
M14	17.6	8.94	37.9	13.9	76.7	54.3
OCW	3.75	3.68	2.70	0.49	25.6	5.02
PIXL	19.1	5.92	36.1	6.15	67.2	35.2
S13	11.1	7.50	22.6	11.5	73.7	54.4
SNF	8.73	5.83	13.7	5.31	55.1	31.9

<sup>a</sup> Average of samples collected from 10/3/00 to 01/31/01.<sup>b</sup> Ratios of the sum of concentrations for seasonal composite to sum of all samples (%).

inversions. To quantitate the seasonal influence upon the annual average, a ratio of the combined late fall and early winter concentrations to the total annual average concentrations is shown in Table 2 as the percent of seasonal contribution to the annual average. The percent of seasonal contribution to the annual average mass concentration for most of the sites was found to be greater than 55% with a maximum of 77%; values above 33% indicate seasonal influence (33% represents an equal contribution of the 4-month period to the annual average mass concentration). CHL and OCW sites, located east of central California, do not show pronounced fall–winter mass contributions, since the values of 21% and 26%, respectively, are lower than 33%. Seasonal contributions to the annual average total carbon (TC) ranged from 5–58%, with a majority of the sites between 30% and 58% (Table 2). Corresponding to the low seasonal mass contribution for CHL and OCW, both sites had a low seasonal to annual TC ratio (9.2% and 5.0%, respectively). Values ranging from 23% to 35% seasonal contribution of annual TC were found for FEL, SNF, HELM, and PIXL. The central California mass concentrations were largely influenced by carbonaceous aerosol. Annual average TC concentrations were found to range from 29% to 166% of the annual average  $\text{PM}_{2.5}$  mass concentration. The maximum value, found for CHL, is likely related to filter absorption artifacts of semi-volatile

organic compounds to quartz filter as compared to Teflon filters (McDow and Huntzicker, 1990). Sites outside the central valley of California (CHL, EDW, and OCW) had very low annual average mass concentrations, a high percentage of which was found to be carbonaceous. Rural central California sites had much lower mass percentages of TC; those sites included COP, FEDL, FEL, and PIXL. Overall the annual average mass and TC concentrations were positively correlated with a Pearson correlation coefficient ( $r^2$ ) of 0.72.

### 3.2. Annual average organic concentrations

Selected organic speciation data from select sites are presented as annual average concentrations in Table 3 and as the weight fraction of TC in Fig. 2 (complete data set is available in Supplemental Information). The annual average TC concentration for each site (13 of 20 sites) was used to normalize the organic compound annual average concentrations to determine the weight fraction. TC was chosen to normalize organic compounds due to differences in OC/EC split obtained by different thermal carbon analytical methods (Chow et al., 2001). This subset of sites was then examined to determine the relative contribution of various organic compound classes to the TC. The most abundant compound class was polar organic compounds (POC). The total POC accounted for

Table 3  
Selected annual average concentrations for the central California sites in  $\text{ng m}^{-3}$

	Bethel Island	China Lake	Fresno Residential	Fresno Supersite	Livermore	Modesto	Olancho	Pixely Wildlife Refuge	Sacramento T Street	SNF Auberry
1,6-Anhydro- $\beta$ -D-mannopyranose (mannosan)	12.23 $\pm$ 1.93	0.44 $\pm$ 0.08	39.53 $\pm$ 6.25	81.27 $\pm$ 12.85	20.28 $\pm$ 3.21	31.43 $\pm$ 4.97	2.86 $\pm$ 0.45	2.67 $\pm$ 0.42	16.89 $\pm$ 2.67	18.88 $\pm$ 2.98
1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan)	49.93 $\pm$ 8.85	7.34 $\pm$ 1.30	121.18 $\pm$ 21.47	201.88 $\pm$ 35.77	67.64 $\pm$ 11.99	100.61 $\pm$ 17.83	13.58 $\pm$ 2.41	19.04 $\pm$ 3.37	62.61 $\pm$ 11.09	56.82 $\pm$ 10.07
1,2-Benzenedicarboxylic (phthalic) acid	3.75 $\pm$ 0.78	1.02 $\pm$ 0.37	4.40 $\pm$ 0.89	9.53 $\pm$ 1.76	3.17 $\pm$ 0.64	6.06 $\pm$ 1.17	2.49 $\pm$ 0.58	4.10 $\pm$ 0.84	3.82 $\pm$ 0.79	3.75 $\pm$ 0.76
1,4-Butanediol (succinic) acid	12.01 $\pm$ 2.44	0.95 $\pm$ 0.36	25.99 $\pm$ 5.12	35.82 $\pm$ 7.01	7.47 $\pm$ 1.53	19.37 $\pm$ 3.84	2.67 $\pm$ 0.66	12.01 $\pm$ 2.44	9.89 $\pm$ 2.03	9.54 $\pm$ 1.95
1,5-Pentanediol (glutaric) acid	3.47 $\pm$ 0.84	1.04 $\pm$ 0.30	7.40 $\pm$ 1.73	10.77 $\pm$ 2.50	2.33 $\pm$ 0.56	5.37 $\pm$ 1.27	1.45 $\pm$ 0.38	2.81 $\pm$ $\pm$ 0.69	2.98 $\pm$ 0.73	2.89 $\pm$ 0.70
1,9-Nonanediol (azelaic) acid	3.15 $\pm$ 0.81	2.69 $\pm$ 0.74	6.00 $\pm$ 1.47	18.74 $\pm$ 4.41	4.14 $\pm$ 1.02	8.11 $\pm$ 1.95	3.77 $\pm$ 0.97	2.28 $\pm$ 0.61	5.25 $\pm$ 1.30	5.56 $\pm$ 1.36
2-Methylbutanedioic (2-methylsuccinic) acid	3.50 $\pm$ 0.80	0.45 $\pm$ 0.17	8.69 $\pm$ 1.91	12.95 $\pm$ 2.82	2.57 $\pm$ 0.58	6.12 $\pm$ 1.36	1.14 $\pm$ 0.30	2.74 $\pm$ 0.64	3.28 $\pm$ 0.75	2.82 $\pm$ 0.65
Hexadecanoic (palmitic) acid	14.05 $\pm$ 11.95	10.09 $\pm$ 12.24	30.66 $\pm$ 19.25	20.81 $\pm$ 14.78	24.25 $\pm$ 14.88	18.30 $\pm$ 13.57	15.80 $\pm$ 13.46	13.00 $\pm$ 11.52	18.86 $\pm$ 14.20	17.84 $\pm$ 13.02
Octadecanoic (stearic) acid	10.24 $\pm$ 9.47	10.68 $\pm$ 11.37	21.08 $\pm$ 14.55	16.60 $\pm$ 12.36	27.01 $\pm$ 16.20	14.97 $\pm$ 11.52	12.22 $\pm$ 11.02	9.91 $\pm$ 9.35	13.52 $\pm$ 11.12	13.97 $\pm$ 10.76
Syringaldehyde	0.58 $\pm$ 0.16	0.02 $\pm$ 0.04	2.75 $\pm$ 0.75	5.23 $\pm$ 1.43	2.72 $\pm$ 0.74	2.53 $\pm$ 0.69	0.11 $\pm$ 0.04	0.06 $\pm$ 0.03	1.14 $\pm$ 0.32	0.52 $\pm$ 0.15
<i>cis</i> -9-hexadecenoic (palmitoleic) acid	0.26 $\pm$ 0.06	0.04 $\pm$ 0.04	0.12 $\pm$ 0.04	0.38 $\pm$ 0.08	0.41 $\pm$ 0.08	0.32 $\pm$ 0.07	0.11 $\pm$ 0.04	0.24 $\pm$ 0.06	0.29 $\pm$ 0.07	0.04 $\pm$ 0.03
<i>cis</i> -9-Octadecenoic (oleic) acid	1.36 $\pm$ 0.50	1.02 $\pm$ 0.40	9.25 $\pm$ 3.18	5.81 $\pm$ 2.02	4.15 $\pm$ 1.44	3.24 $\pm$ 1.14	0.69 $\pm$ 0.28	0.97 $\pm$ 0.37	3.09 $\pm$ 1.09	1.13 $\pm$ 0.42
Dehydroabietic acid	8.91 $\pm$ 1.20	0.02 $\pm$ 0.61	0.00 $\pm$ 0.02	19.86 $\pm$ 2.16	13.52 $\pm$ 1.49	9.64 $\pm$ 1.24	5.88 $\pm$ 0.99	0.16 $\pm$ 0.46	9.93 $\pm$ 1.29	15.35 $\pm$ 1.72
Cholesterol	0.00 $\pm$ 0.04	0.00 $\pm$ 0.03	0.11 $\pm$ 0.07	0.00 $\pm$ 0.02	1.53 $\pm$ 0.54	0.01 $\pm$ 0.04	0.00 $\pm$ 0.04	0.00 $\pm$ 0.02	1.83 $\pm$ 0.65	0.07 $\pm$ 0.05
Retene	0.11 $\pm$ 0.04	0.06 $\pm$ 0.04	0.37 $\pm$ 0.06	0.41 $\pm$ 0.06	0.10 $\pm$ 0.03	0.08 $\pm$ 0.03	0.09 $\pm$ 0.04	0.07 $\pm$ 0.04	0.08 $\pm$ 0.04	0.25 $\pm$ 0.05
Benz(a)anthracene	0.03 $\pm$ 0.07	0.02 $\pm$ 0.09	0.15 $\pm$ 0.07	0.02 $\pm$ 0.06	0.07 $\pm$ 0.05	0.10 $\pm$ 0.07	0.04 $\pm$ 0.08	0.03 $\pm$ 0.07	0.04 $\pm$ 0.07	0.05 $\pm$ 0.06
Chrysene & triphenylene	0.18 $\pm$ 0.05	0.03 $\pm$ 0.05	0.28 $\pm$ 0.06	0.10 $\pm$ 0.04	0.22 $\pm$ 0.04	0.36 $\pm$ 0.07	0.11 $\pm$ 0.05	0.17 $\pm$ 0.05	0.16 $\pm$ 0.04	0.25 $\pm$ 0.05
Indeno[123-cd]pyrene	0.09 $\pm$ 0.07	0.02 $\pm$ 0.09	0.25 $\pm$ 0.08	0.07 $\pm$ 0.06	0.05 $\pm$ 0.05	0.27 $\pm$ 0.08	0.06 $\pm$ 0.07	0.10 $\pm$ 0.07	0.10 $\pm$ 0.07	0.05 $\pm$ 0.06
Benzo[ghi]perylene	0.24 $\pm$ 0.09	0.04 $\pm$ 0.11	0.67 $\pm$ 0.15	0.68 $\pm$ 0.15	0.21 $\pm$ 0.07	0.48 $\pm$ 0.12	0.09 $\pm$ 0.09	0.14 $\pm$ 0.09	0.21 $\pm$ 0.09	0.32 $\pm$ 0.09
Coronene	0.11 $\pm$ 0.03	0.02 $\pm$ 0.03	0.27 $\pm$ 0.05	0.25 $\pm$ 0.04	0.10 $\pm$ 0.02	0.18 $\pm$ 0.03	0.04 $\pm$ 0.03	0.07 $\pm$ 0.03	0.10 $\pm$ 0.03	0.14 $\pm$ 0.03
20R 5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-Cholestane &	0.03 $\pm$ 0.03	0.04 $\pm$ 0.04	0.08 $\pm$ 0.03	0.06 $\pm$ 0.03	0.05 $\pm$ 0.02	0.05 $\pm$ 0.03	0.02 $\pm$ 0.03	0.05 $\pm$ 0.03	0.04 $\pm$ 0.03	0.02 $\pm$ 0.02
20S13B(H), 17 $\alpha$ (H)-Diasterane										
Gravimetric mass <sup>a</sup>	8.57 $\pm$ 1.66	2.29 $\pm$ 1.56	24.18 $\pm$ 2.20	25.27 $\pm$ 2.25	10.79 $\pm$ 1.70	17.56 $\pm$ 1.96	3.75 $\pm$ 1.61	19.10 $\pm$ 1.93	11.10 $\pm$ 1.68	8.73 $\pm$ 1.62
Total carbon <sup>a</sup>	4.08 $\pm$ 1.23	3.81 $\pm$ 1.32	11.30 $\pm$ 1.74	13.61 $\pm$ 1.88	6.80 $\pm$ 1.42	8.94 $\pm$ 1.60	3.68 $\pm$ 1.29	5.92 $\pm$ 1.41	7.50 $\pm$ 1.49	5.83 $\pm$ 1.42

<sup>a</sup>Concentration in  $\mu\text{g m}^{-3}$ .

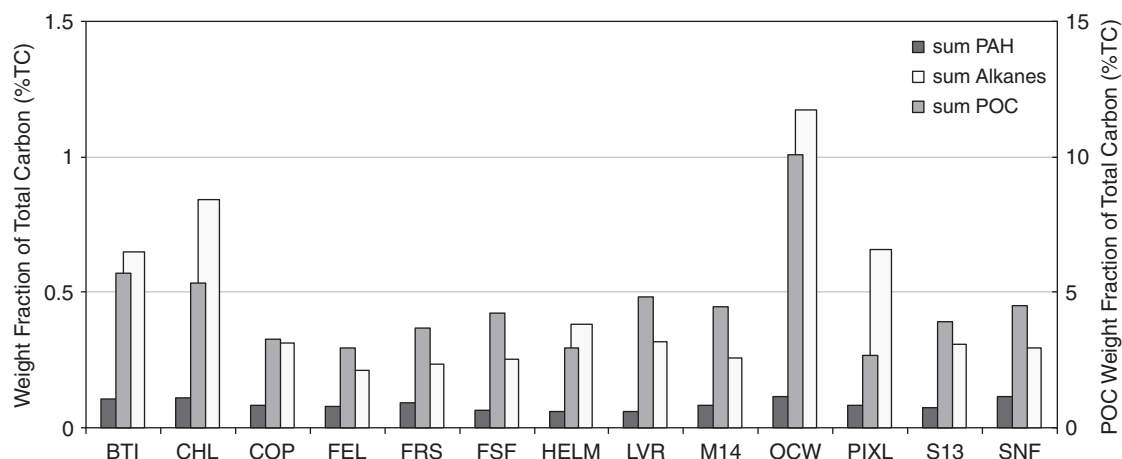


Fig. 2. Total carbon weight fractions of organic compounds.

3–10% of the TC, while the total alkanes accounted for 0.2–1.2%, and the total PAH accounted for 0.05–0.1% (Fig. 2). This class of compounds includes both components of primary emissions and secondary formation products.

Due to insufficient data for three sites and no sample collection for carbon analysis at four sites, the normalized dataset is limited to 13 of the 20 sites; hence, annual average concentrations without normalization to TC are discussed. It should be noted that annual average concentrations were reported after blank subtraction and that blanks were found to have some contamination from impactor grease used in mini-vol samplers. A complete list of field blank concentrations for all organic compounds is provided in the Supplemental Information.

### 3.2.1. Polar organic compounds

A total of 56 POC, including several unique molecular markers for biomass combustion, are reported in a Supplemental Table. The compound class also includes a variety of organic acids which are abundant in the atmosphere and in PM<sub>2.5</sub> source emissions (Simoneit and Mazurek, 1982; Rogge et al., 1991; Rogge et al., 1993b; Chebbi and Carlier, 1996; Nolte et al., 2001). Total POC concentrations were 30–40 times higher than total PAH concentrations. The most abundant compounds include levoglucosan, mannosan, alkanolic acids such as palmitic and oleic acids, and alkanedioic acids such as succinic and azelaic acids. The sources of alkanolic and alkanedioic acids include both natural and anthropogenic emission sources. The percen-

tage of alkanolic acids to the total POC concentration varies from 11% at FSF to 65% at YOSE. The fraction of alkanedioic acids varied from less than 10% at LVR to 25% at HELM. The percentage of sugar anhydrides, levoglucosan and mannosan, varied from less than 5% at the FEL and YOSE to 50% at the FSF. The sum of these three subgroups, alkanedioic and alkanolic acids and sugar anhydrides comprised 70–88% of the POC quantitated. These intra-site differences are likely related to anthropogenic and biogenic emission source differences. A comparison of S13 and OCW, (urban and rural site, respectively) provides an example of these site differences (Fig. 3). Sugar anhydrides accounted for 38% of the total annual average POC at S13, and 12% at OCW. Alkanolic acids were also quite different between the two sites with values of 31% and 56% of the total POC for S13 and OCW, respectively. However, the fraction of *n*-alkanedioic acids of the total POC at both sites was relatively constant (9% and 11% for OCW and S13, respectively). OCW had much lower influence of fall–winter season on the mass (25%) and total carbon (5%) concentration, in contrast to S13 (74% and 54%, respectively).

Biomass combustion is an important source of PM<sub>2.5</sub>. There are several sources of biomass combustion within central California, such as: wildland fires in the Sierra Nevada mountain range occurring naturally and by prescription in the summer and fall, agricultural burning for waste reduction that takes place in the fall by locally issued permits, and winter residential wood combustion. From the analysis of fall–winter mass and

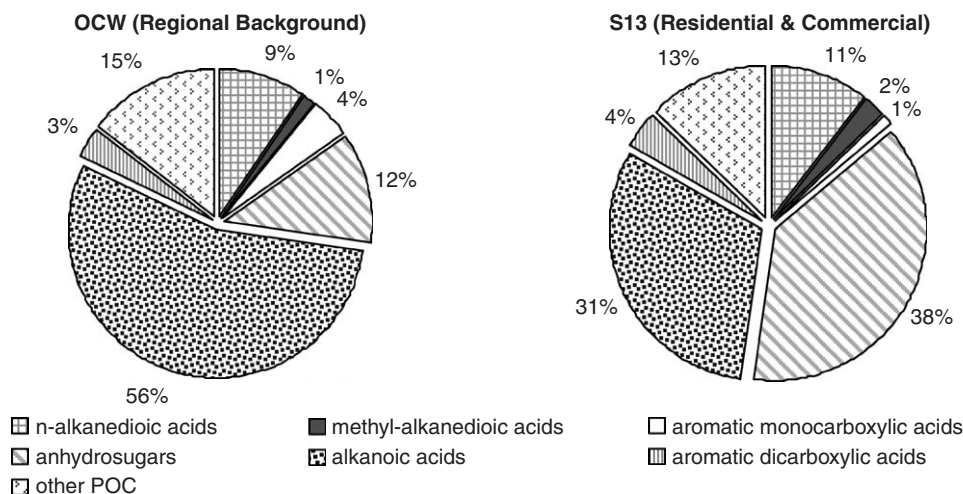


Fig. 3. POC compound subgroups as percent of total POC.

carbon contributions (Table 2), it is reasonable to assume that the majority of the biomass combustion for most sites occurred during the fall and winter period and was likely related to agricultural burning and residential wood combustion. Unique molecular markers for wood combustion include levoglucosan, mannosan, syringaldehyde, eugenol, dehydroabietic acid and retene. These compounds were positively correlated with each other in varying degrees due to common sources. Low annual average concentrations of syringaldehyde, eugenol, dehydroabietic acid, and retene were recorded at several sites. The correlation between levoglucosan and mannosan was very strong ( $r^2 = 0.97$ ) as was expected due to common sources of these compounds (Zdrahal et al., 2002) and high relative annual average concentration at many sites. The  $r^2$  for syringaldehyde and levoglucosan was 0.72 while eugenol did not correlate with levoglucosan ( $r^2 = 0.08$ ); the low correlation coefficient may be due to the semi-volatile nature of eugenol (Hawthorne et al., 1989). Dehydroabietic acid was strongly correlated to retene due to their similar origin, mainly coniferous woods (Simoneit et al., 1993; Elias et al., 2001), while both were moderately correlated to levoglucosan, which is found in both coniferous and deciduous woods. The highest values of these molecular markers were found in Fresno. Levoglucosan and mannosan account for 1.4–2.1% of the TC for FRS and FSF, respectively. The annual average concentrations of levoglucosan were 120 and 200  $\text{ng m}^{-3}$  in FRS and FSF, respectively. In previous studies levoglucosan concentrations up

to 7600  $\text{ng m}^{-3}$  were reported for Fresno during winter episode sampling periods (Schauer and Cass, 2000; Poore, 2002). Peak levoglucosan concentrations may have been missed in this study, due to every sixth day sampling; however, levoglucosan was the most abundant  $\text{PM}_{2.5}$  associated organic compound found in central California.

Although the sources of dicarboxylic acids include secondary organic aerosol formation reactions (Kawamura and Gagosian, 1987; Grosjean and Seinfeld, 1989; Chebbi and Carlier, 1996; Kawamura et al., 1996; Keywood et al., 2004a,b) it seems that the majority of these compounds correlate with markers of anthropogenic emission sources. For example, alkanedioic acids correlated with levoglucosan, but not with alkanolic acids.  $R^2$  values ranged from 0.70 to 0.83 for levoglucosan versus succinic, methylsuccinic, glutaric, and azelaic acids. Succinic acid was the most abundant alkanedioic acid followed by azelaic acid in most sites. Succinic acid has been found in vehicular emissions (Kawamura and Kaplan, 1987; Fujita et al., 2005) and in oak wood combustion (Rogge et al., 1998). Phthalic acid, possibly related to secondary atmospheric reactions (Fine et al., 2004), correlated ( $r^2 = 0.85$ ) with succinic acid. However, phthalic acid has also been found in vehicular exhaust (Fraser et al., 2003; Fujita et al., 2005). Both succinic and phthalic acid were weakly correlated to vehicular molecular markers, however, the correlations were not strong enough to indicate vehicle emissions as a major source of these compounds.



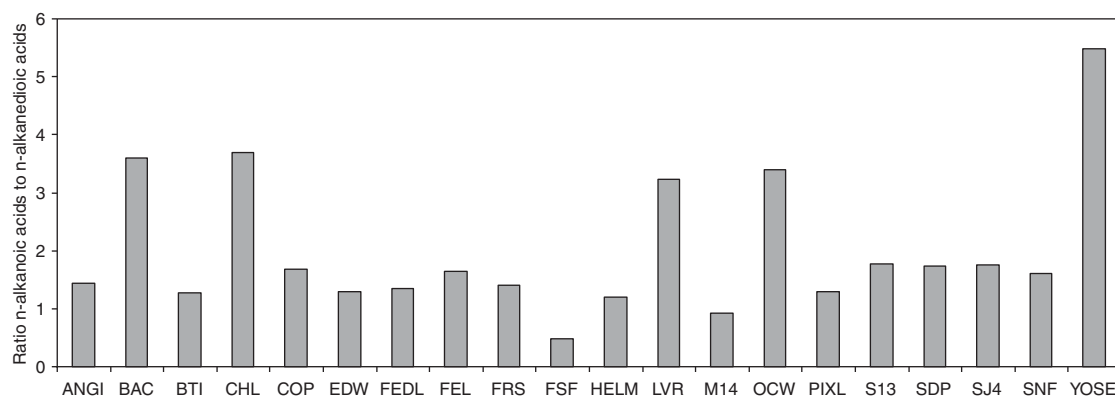


Fig. 4. Ratios of *n*-Alkanoic acids to *n*-Alkanedioic acids for the annual average sites.

Alkanoic acids were prevalent throughout the valley. Alkanoic acids appear to originate from different emission sources or precursors than alkanedioic acids. Highest alkanoic acid concentrations were found in BAC, FEDL, FRS, LVR, SDP, and YOSE. The highest concentrations of *n*-alkanedioic acids were found in FSF (Fresno 1st Street). The ratio of alkanoic to alkanedioic acids for most sites ranged from 1 to 2 (Fig. 4), however BAC, CHL, LVR, OCW had ratios greater than 3, with a maximum of 5 for YOSE. The minimum ratio, 0.5 for FSF, may be related to low biogenic alkanoic acid input. Carbon preference index (CPI) provides an indication of the origin of monocarboxylic acids (Simoneit and Mazurek, 1982; Simoneit, 1989; Zheng et al., 2000). Described by Simoneit (1989), biogenic *n*-alkanoic acids have a definite even-to-odd bias due to enzyme-regulated biosynthesis. The overall CPI of *n*-alkanoic acids ( $C_6$ – $C_{21}$ ) was  $3 \pm 0.4$ . CPI values in central California were lower than those reported by Zheng et al. (2000) for Hong Kong  $PM_{10}$  aerosol (4–23) and lower than those reported by Simoneit (1989) for aerosol in China (4–15). The low variance of the alkanoic acid CPI within central California indicates spatial uniformity of emission sources for these compounds.

Oleic acid, palmitoleic acid, and cholesterol, proposed molecular markers for meat cooking (Schauer et al., 1999b), did not correlate. This is likely due to their high atmospheric oxidation susceptibility (Kawamura and Gagosian, 1987). After removal of the high values for ANGI, FEL, and COP, a correlation ( $r^2 = 0.88$ ) between oleic acid and eladic acid was found. However, the correlation between cholesterol and oleic acid did not improve. This is not surprising, since annual

average concentrations of cholesterol were below method detection limits at many sites and oleic acid has also been found in leaf abrasion products (Rogge et al., 1993b). The vegetative matter as a source for oleic acid could explain the high values found in ANGI, FEL, and COP. The ratio of oleic acid to azelaic acid for those three sites and FRS, LVR, and YOSE were all one or greater, while most of the remaining site ratios were 0.5 or less. Since azelaic acid may be a reaction product from oxidation of the oleic acid and other compounds, the high ratio may be an indication of a high input of vegetative matter compared to other sources.

Fraser et al. (2003) suggested that palmitic and stearic acids are highly correlated in part because of meat-cooking emissions. In this study, palmitic acid also correlated well with many alkanoic acids and was one of the most abundant constituents of this compound class. Palmitic acid and stearic acids are abundant in ambient aerosol and are found in many emission sources (Rogge et al., 1991; Schauer et al., 1999b; Schauer et al., 2002b). Meat cooking could not be easily distinguished from other emission sources in this dataset.

### 3.2.2. Polycyclic aromatic hydrocarbons

Reported in the Supplemental Table are 55 high molecular weight PAH including alkyl-PAH. This group of compounds was the least abundant in terms of their contribution to TC, but they included many distinctive molecular markers of vehicular exhaust and wood smoke. The average concentration of total PAH among the 20 sites was  $5.6 \pm 2 \text{ ng m}^{-3}$ . The highest concentrations were found in urban areas such as FRS, FSF, BAC and M14. The lowest concentrations were found at HELM, EDW, ANGI, FEL, and LVR. The total

PAH correlated with the total POC ( $r^2 = 0.63$ ), but not with the total alkanes ( $r^2 = 0.15$ ). The largest subgroup of POC, the sugar anhydrides, correlated with total PAH ( $r^2 = 0.59$ ).

PAH are emitted as a result of incomplete combustion: sources include biomass combustion emissions (Oros and Simoneit, 1999; McDonald et al., 2000; Schauer et al., 2001; Hays et al., 2002), vehicular emissions (Rogge et al., 1993a; Schauer et al., 1999a; Schauer et al., 2002a; Zielinska et al., 2004a,b), and industrial emissions (Rogge et al., 1997; England et al., 2000). Individual high molecular weight particle-phase PAH present in higher relative abundance to total PAH in source emissions (Zielinska et al., 2004b; Fujita et al., 2005) may indicate vehicle emission source contributions to the annual average sites. Gasoline vehicles had high abundances of coronene, indeno(1,2,3-*cd*)pyrene, and benzo(ghi)perylene (Miguel et al., 1998; Zielinska et al., 2004a,b). Elevated ratios of these molecular marker compounds to total PAH indicate the significance of vehicular pollution, due to their higher relative abundance in gasoline vehicle emissions compared to other combustion emissions. The maximum ratio of benzo(ghi)perylene to total PAH was 0.08 at FSF followed by FRS, SJ4, SDP, and M14. High values near 0.05 were found also at BAC, BTI, SNF, and FEL and lower ratios were measured at HELM, ANGI, OCW and CHL in decreasing order. The ratios of coronene to total PAH had less variance between the maximum at SJ4 and the minimum at CHL. Coronene correlated with benzo(ghi)perylene ( $r^2 = 0.87$ ) with the exception of one outlier at SJ4. Source emissions of diesel vehicles have shown an abundance of benz(a)anthracene and chrysene + triphenylene (Zielinska et al., 2004a,b). The two compounds correlated well at all sites except FRS and FSF. Both sites had a high concentration of benz(a)anthracene, but unexpected low chrysene + triphenylene concentration. Due to these unexpected lows, the benz(a)anthracene to total PAH ratios was used to indicate contributions of diesel emission to the annual average sites. The peak ratio was 0.06 at FSF followed by FRS, SDP, and SNF. Values of approximately 0.04 were found at BAC, M14, SJ4, BTI and LVR. The minimum value of less than 0.01 was found at CHL followed by ANGI and HELM. The ratios of benz(a)anthracene to total PAH correlated with the ratios of benzo(ghi)perylene to total PAH among the annual average sites ( $r^2 = 0.79$ ). This might indicate a relative similar

significance of gasoline and diesel vehicle emissions at corresponding annual average sites.

### 3.2.3. Alkanes

High molecular weight alkanes ( $C_{16}$ – $C_{36}$ ) were found at each site. The alkanes are less abundant than POC, but are on average 2–10 times more abundant than PAH. The total alkane concentration varied more among sites than total PAH and POC. The average total alkane concentration was  $30 \pm 10 \text{ ng m}^{-3}$ . The total alkane concentrations among the sites did not correlate well with total concentrations of POC or PAH. Alkanes arise from both anthropogenic and biogenic sources. The alkane CPI is defined as the sum of the odd carbon number homologs divided by the even carbon number homologs. Generally, alkanes with a CPI close to 1 are thought to arise from anthropogenic sources while higher CPI values indicate a biogenic origin. The overall CPI for  $C_{17}$ – $C_{36}$  alkanes was on average  $1.7 \pm 0.3$ . The alkanes can be broken into two subsets one with low carbon preference index (LCPI) for combustion emission sources and a second with high carbon preference index (HCPI) for vegetative matter contributions (Bourbonniere et al., 1997). The LCPI for  $C_{17}$ – $C_{26}$  was on average  $1.2 \pm 0.2$ , while the HCPI for  $C_{25}$ – $C_{36}$  was  $2.0 \pm 0.4$ . These CPIs indicate particulate contributions from both vehicular and vegetative matter sources. The fraction of alkane related to vegetative wax may be estimated for each site by:  $\text{Wax } C_n = [C_n] - [((C_{n+1}) + (C_{n-1}))/2]$ , where  $C_n$  are individual alkanes and  $n$  is the chain length. Negative values for  $\text{Wax } C_n$  were taken as zero, as done by Simoneit et al. (1991). Positive values of  $\text{Wax } C_n$  for alkane series ( $C_{16}$ – $C_{36}$ ) were added and divided by the total alkanes to obtain the fraction of alkane associated with vegetative wax. The annual average plant wax alkane was 22–39% of the total. The  $C_{\text{max}}$  and second  $C_{\text{max}}$  were  $C_{31}$  and  $C_{29}$  consistently for all sites, providing further evidence of vegetative input.

Since the overall CPI was near one for most sites and 64–75% of the alkanes were not from plant waxes, it may be assumed that the remaining alkanes were related to vehicular emissions. However, the alkanes were not found to correlate with the vehicular molecular markers. In addition levoglucosan, a marker for wood smoke found in high concentrations in central California, was not well correlated to alkanes. Since the spatial distribution of the high molecular weight alkanes did

not correlate to molecular markers for vehicular emissions or biomass combustion, it may be concluded that alkanes originate from many different sources.

#### 3.2.4. Hopanes and steranes

Hopanes concentrations did not pass critical validation steps due to a strong GC/MS interferences originating from impactor grease used in mini-vol sampling. However, steranes were not affected by the impactor grease interferences. Both hopanes and steranes are found in lubricating oils used in engine combustion and have been found in vehicle exhaust (Zielinska et al., 2004a,b). 20R5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-cholestane and 20S13 $\beta$ (H), 17 $\alpha$ (H)-diasterane were found to be weakly correlated with phytane ( $r^2 = 0.37$ ) both concentrations were too low to be well fitted by linear regression. Phytane, an isoprenoid has been reported to be associated with diesel emissions (Schauer et al., 1999a).

#### 3.3. Spatial distribution of particulate organic compounds in central California

The annual average concentrations of individual organic species within three compound classes (i.e. POC, PAH and alkanes) were highly correlated among several central California sites. This correlation may indicate that the pollution sources and/or pollution transport were similar for the year 2000 at several of the annual average sites. However, the individual organic compounds measured at the two Fresno sites did not correlate well to other central California sites. These two sites, FSF and FRS were highly correlated with each other, but neither were well correlated with any of the upwind sites. Residential (FRS) and supersite (FSF) PAH annual average concentrations had the highest degree of correlation for the 55 individual PAH compounds ( $r^2 = 0.92$ ) compared to other sites, likely because of the close proximity and similar local emission sources. These two sites had slightly lower correlation coefficients for POC ( $r^2 = 0.76$ ) and alkanes ( $r^2 = 0.87$ ).

Correlations of POC concentrations between most other sites were strongest. Also strongly correlated among sites were the *n*-alkane concentrations. PAH concentrations were correlated between a few sites, but less so than POC and *n*-alkanes. The decrease in correlation of PAH may be related to differences in local emission sources. Several up-

wind sites, BTI, LVR, M14, SDP, and SJ4 correlated well with S13 with correlation coefficients ( $r^2$ ) ranging from 0.7 to 1. In addition, SNF and COP correlated strongly to one or more of the upwind sites. SNF, a rural site in the foothills of the Sierra Nevada Mountains, was strongly correlated to BTI, LVR, M14, and S13. In each of these correlations, the PAH were less well correlated than POC and alkanes.

#### 4. Conclusions

Annual mean PM<sub>2.5</sub> mass concentrations that were derived from year round sixth day 24-h samples were dominated by fall–winter samples collected between October 3, 2000 and January 31, 2001, for many (but not all) sites. During this time many central California sites had 24-h PM<sub>2.5</sub> mass concentrations exceeding the 24-h NAAQS. The highest 24-h concentration of 175  $\mu\text{g m}^{-3}$  was found in Fresno on January 1, 2001. The most abundant particulate phase organic compounds identified were polar organic compounds (POC). Sugar anhydrides, molecular markers of wood combustion, constituted the largest weight fraction of TC, followed by alkanic acids, and alkanedioic acids. High molecular weight alkanes were the next most abundant class of compounds. Approximately 30% of the alkanes quantitated were found to originate from plant wax. Fifty five PAH's were identified in this study, all in low annual average concentrations compared to POC and alkanes. PAH were found in highest concentrations at sites with high vehicular and wood smoke emissions.

Emission source molecular markers varied among sites. Levoglucosan and mannosan were highest at FSF followed by FRS, SDP, M14, LVR and S13 and low at FEL, CHL, YOSE, EDW, OCW, HELM, and PIXL. Additional biomass combustion markers, syringaldehyde, dehydroabietic acid, and retene correlated with levoglucosan. Spatial differences between alkanic acids and alkanedioic acids indicate that these compounds arise from different emission sources and/or volatile precursors emitted from different sources. Although the origin of alkanedioic acids remains uncertain, they appeared to be related to anthropogenic emissions, especially succinic and phthalic acid, although their atmospheric formation cannot be ruled out. While alkanedioic acids correlated with levoglucosan, alkanic acids did not, suggesting that alkanedioic acids either are emitted in urban areas or are closely

related to anthropogenic emissions. Molecular markers for gasoline and diesel emissions, benzo(ghi)perylene and benzo(a)anthracene varied among the sites and showed an increased relative abundance compared with total PAH at sites with expected vehicle emission influence including: FSF, FRS, SDP, and SJ4. Relationships between typical molecular markers for meat cooking and emission sources were not evident in this study. High-molecular weight alkanes were found at all of the central California sites. CPI and plant wax calculations suggest a moderate influence of vegetative matter relative to other winter emission sources at many of the central California sites.

The annual average concentrations of individual organic species within compound classes were largely correlated. Many sites, BTI, LVR, M14, SDP, SJ4, COP and SNF correlated with S13. Many of these sites are in close proximity with similar local sources to S13 except SNF and COP. These correlations provide an indication of the pollution stagnation and average transport of PM<sub>2.5</sub> emission sources. The two Fresno sites (FRS and FSF) correlated with each other especially with respect to PAH, but did not correlate to other central California sites.

## Acknowledgements

The authors would like to thank Barbara Hinsvark and Steve Kohl for their management of annual average filter collection and bulk laboratory analyses, Don Lehrman for management of the Fresno Supersite, and John Watson and anonymous reviewers for their helpful review of this manuscript.

## Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.atmosenv.2005.09.035](https://doi.org/10.1016/j.atmosenv.2005.09.035)

## References

- Bevington, P.R., 1969. Reduction and Error Analysis for the Physical Sciences. McGraw Hill, New York.
- Bourbonniere, R.A., Telford, S.L., Ziolkowski, L.A., Lee, J., Evans, M.S., Meyers, P.A., 1997. Biogeochemical marker profiles in cores of dated sediments from large North American lakes. In: Eganhouse, R.P. (Ed.), Biogeochemical marker profiles in cores of dated sediments from large North American lakes, vol. 671. American Chemical Society, Washington, DC, pp. 133–150.
- Chebbi, A., Carlier, P., 1996. Carboxylic acids in the troposphere, occurrence, sources, and sinks: a review. *Atmospheric Environment* 30 (24), 4233–4249.
- Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The DRI thermal optical reflectance carbon analysis system—description, evaluation and applications in United-States air-quality studies. *Atmospheric Environment Part A-General Topics* 27 (8), 1185–1201.
- Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merrifield, T., 2001. Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Science and Technology* 34 (1), 23–34.
- Elias, V.O., Simoneit, B.R.T., Cordeiro, R.C., Turcq, B., 2001. Evaluating levoglucosan as an indicator of biomass burning in Carajas, Amazonia: a comparison to the charcoal record. *Geochimica et Cosmochimica Acta* 65 (2), 267–272.
- El-Zanan, H.S., Zielinska, B., Rinehart, L.R., Hansen, D.A., 2005. Measurement of the aerosol organic mass to organic carbon ratio and chemical characterization of atmospheric aerosol in support of Atlanta health study: Particle and multiphase organics. *Journal of the Air and Waste Management Association*, submitted for publication.
- England, G.C., Zielinska, B., Loos, K., Crane, I., Ritter, K., 2000. Characterizing PM<sub>2.5</sub> emission profiles for stationary sources: comparison of traditional and dilution sampling techniques. *Fuel Processing Technology* 65, 177–188.
- EPA US, 2005. Map of Nonattainment Areas.
- Fine, P.M., Shen, S., Sioutas, C., 2004. Inferring the sources of fine and ultrafine particulate matter at downwind receptor sites in the Los Angeles basin using multiple continuous measurements. *Aerosol Science and Technology* 38, 182–195.
- Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 2003. Air quality model evaluation data for organics. 6. C-3-C-24 organic acids. *Environmental Science and Technology* 37 (3), 446–453.
- Fujita, E.M., Zielinska, B., Campbell, D., Arnott, W.P., Sagebiel, J.C., Chow, J.C., Rinehart, L.R., Gabele, P.A., Crews, W., Snow, R., Clark, N.N., Wayne, S., Lawson, D.R., 2005. Variations in speciated emissions from spark-ignition and compression-ignition motor vehicles in the California's south coast air basin. *Journal of the Air and Waste Management Association*, submitted for publication.
- Grosjean, D., Seinfeld, J.H., 1989. Parameterization of the formation potential of secondary organic aerosols. *Atmospheric Environment* 23 (8), 1733–1747.
- Hawthorne, S.B., Krieger, M.S., Miller, D.J., Mathiason, M.B., 1989. Collection and quantitation of methoxylated phenol tracers for atmospheric pollution from residential wood stoves. *Environmental Science and Technology* 23 (4), 470–475.
- Hays, M.D., Geron, C.D., Linna, K.J., Smith, N.D., Schauer, J.J., 2002. Speciation of gas-phase and fine particle emissions from burning of foliar fuels. *Environmental Science and Technology* 36 (11), 2281–2295.
- Kawamura, K., Gagosian, R.B., 1987. Implications of omega-oxocarboxylic acids in the remote marine atmosphere for photooxidation of unsaturated fatty-acids. *Nature* 325 (6102), 330–332.
- Kawamura, K., Kaplan, I.R., 1987. Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air. *Environmental Science and Technology* 21 (1), 105–110.

- Kawamura, K., Kasukabe, H., Barrie, L.A., 1996. Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: one year of observations. *Atmospheric Environment* 30 (10–11), 1709–1722.
- Keywood, M.D., Kroll, J.H., Varutbangkul, V., Bahreini, R., Flagan, R.C., Seinfeld, J.H., 2004a. Secondary organic aerosol formation from cyclohexene ozonolysis: effect of OH scavenger and the role of radical chemistry. *Environmental Science and Technology* 38 (12), 3343–3350.
- Keywood, M.D., Varutbangkul, V., Bahreini, R., Flagan, R.C., Seinfeld, J.H., 2004b. Secondary organic aerosol formation from the ozonolysis of cycloalkenes and related compounds. *Environmental Science and Technology* 38 (15), 4157–4164.
- Manchester-Neesvig, J.B., Schauer, J.J., Cass, G.R., 2003. The distribution of particle-phase organic compounds in the atmosphere and their use for source apportionment during the southern California children's health study. *Journal of the Air and Waste Management Association* 53 (9), 1065–1079.
- McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., Watson, J.G., 2000. Fine particle and gaseous emission rates from residential wood combustion. *Environmental Science and Technology* 34 (11), 2080–2091.
- McDow, S.R., Huntzicker, J.J., 1990. Vapor adsorption artifact in the sampling of organic aerosol: face velocity effects. *Atmospheric Environment Part A-General Topics* 24 (10), 2563–2571.
- Miguel, A.H., Kirchstetter, T.W., Harley, R.A., Hering, S.V., 1998. On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. *Environmental Science and Technology* 32 (4), 450–455.
- Nolte, C.G., Schauer, J.J., Cass, G.R., Simoneit, B.R.T., 2001. Highly polar organic compounds present in wood smoke and in the ambient atmosphere. *Environmental Science and Technology* 35 (10), 1912–1919.
- Oros, D.R., Simoneit, B.R.T., 1999. Identification of molecular tracers in organic aerosols from temperate climate vegetation subjected to biomass burning. *Aerosol Science and Technology* 31 (6), 433–445.
- Pinto, J.P., Lefohn, A.S., Shadwick, D.S., 2004. Spatial variability of PM<sub>2.5</sub> in urban areas in the United States. *Journal of the Air and Waste Management Association* 54 (4), 440–449.
- Poore, M.W., 2002. Levoglucosan in PM<sub>2.5</sub> at the Fresno supersite. *Journal of the Air and Waste Management Association* 52 (1), 3–4.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1991. Sources of fine organic aerosol—1. Charbroilers and meat cooking operations. *Environmental Science and Technology* 25 (6), 1112–1125.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993a. Sources of fine organic aerosol 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environmental Science and Technology* 27 (4), 636–651.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993b. Sources of fine organic aerosol—4. Particulate abrasion products from leaf surfaces of urban plants. *Environmental Science and Technology* 27 (13), 2700–2711.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1997. Sources of fine organic aerosol 8. Boilers burning No. 2 distillate fuel oil. *Environmental Science and Technology* 31 (10), 2731–2737.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1998. Sources of fine organic aerosol—9. Pine, oak, and synthetic log combustion in residential fireplaces. *Environmental Science and Technology* 32 (1), 13–22.
- Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environmental Science and Technology* 34 (9), 1821–1832.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999a. Measurement of emissions from air pollution sources 2. C<sub>1</sub> through C<sub>30</sub> organic compounds from medium duty diesel trucks. *Environmental Science and Technology* 33 (10), 1578–1587.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999b. Measurement of emissions from air pollution sources: C<sub>1</sub> through C<sub>29</sub> organic compounds from meat charbroiling. *Environmental Science and Technology* 33 (10), 1566–1577.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2001. Measurement of emissions from air pollution sources 3. C<sub>1</sub>–C<sub>29</sub> organic compounds from fireplace combustion of wood. *Environmental Science and Technology* 35 (9), 1716–1728.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002a. Measurement of emissions from air pollution sources 5. C<sub>1</sub>–C<sub>32</sub> organic compounds from gasoline-powered motor vehicles. *Environmental Science and Technology* 36, 1169–1180.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002b. Measurement of emissions from air pollution sources. 4. C<sub>1</sub>–C<sub>27</sub> organic compounds from cooking with seed oils. *Environmental Science and Technology* 36 (4), 567–575.
- Simoneit, B.R.T., 1989. Organic matter of the troposphere-V: Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. *Journal of Atmospheric Chemistry* 8, 251–275.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the troposphere II—Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmospheric Environment* 16 (9), 2139–2159.
- Simoneit, B.R.T., Sheng, G.Y., Chen, X.J., Fu, J.M., Zhang, J., Xu, Y.P., 1991. Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atmospheric Environment* 25 (10), 2111–2129.
- Simoneit, B.R.T., Rogge, W.F., Mazurek, M.A., Standley, L.J., Hildemann, L.M., Cass, G.R., 1993. Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Environmental Science and Technology* 27 (11), 2533–2541.
- Watson, J.G., Chow, J.C., 2002a. Comparison and evaluation of in situ and filter carbon measurements at the Fresno Supersite. *Journal of Geophysical Research-Atmospheres* 107 (D21).
- Watson, J.G., Chow, J.C., 2002b. A wintertime PM<sub>2.5</sub> episode at the Fresno, CA, supersite. *Atmospheric Environment* 36 (3), 465–475.
- Zdrahal, Z., Oliveira, J., Vermeylen, R., Claeys, M., Maenhaut, W., 2002. Improved method for quantifying levoglucosan and related monosaccharide anhydrides in atmospheric aerosols



- and application to samples from urban and tropical locations. *Environmental Science and Technology* 36 (4), 747–753.
- Zheng, M., Fang, M., Wang, F., To, K.L., 2000. Characterization of the solvent extractable organic compounds in PM<sub>2.5</sub> aerosols in Hong Kong. *Atmospheric Environment* 34 (17), 2691–2702.
- Zielinska, B., Sagebiel, J., Arnott, W.P., Rogers, C.F., Kelly, K.E., Wagner, D.A., Lighty, J.S., Sarofim, A.F., Palmer, G., 2004a. Phase and size distribution of polycyclic aromatic hydrocarbons in diesel and gasoline vehicle emissions. *Environmental Science and Technology* 38 (9), 2557–2567.
- Zielinska, B., Sagebiel, J., McDonald, J.D., Whitney, K., Lawson, D.R., 2004b. Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *Journal of the Air and Waste Management Association* 54 (9), 1138–1150.